

Competitive growth of crystalline form II and form I in isotactic Polybutene-1



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HIGHLIGHTS

- The competitive growth of form I and II can be classified into three regimes based on the crystallinity of form II.
- Nucleation of form I will be initiated only when the internal stress is sufficient.
- Both increasing the lamella thickness and decreasing the regularity of form II accelerate the transformation from form II to I.

ABSTRACT

The competitive growth of form II and form I in isotactic polybutene-1 (PB-1) was investigated with fast scanning chip calorimetry. By systematically varying the isothermal time, the pre-crystallized PB-1 samples with different crystallinity of form II are obtained and then used to study the competition between the growth of form II and the transformation of form II into form I. All the samples were annealed at 258 K for 60s to help nucleation of form I so that fast transformation could be performed. Crystal transformation kinetics results indicated that the competitive growth of form II and form I can be classified into three regimes. When the crystallinity of form II is small enough, fast transformation from form II to form I does not take place, attributed to lacking of the nuclei of form I as the degree of internal stress is extremely low. This suggests that only certain strength of internal stress and certain crystallinity of form II enable the nucleation of form I and then promote the transformation from form II to form I. With increasing crystallinity of form II, both fast transformation and slow transformation are observed. When crystallinity of form II further increases, only fast transformation is observed. However, the transition rate decreases and then reaches a plateau, resulting from the rearrangement of polymer chains and the increasing regularity of form II, indicating that the increasing regularity of form II inhibits the transformation from form II to form I.

1. Introduction

Isotactic polybutene-1 (PB-1) is a thermoplastic material of industrial interest in the field of water pipes as a substitute for poly (vinyl chloride) due to its comparatively good chemical/heat resistance and free from the elution of endocrine disruptor. PB-1 contains four crystalline forms: twined hexagonal form I, untwined hexagonal/trigonal form I' [1,2], tetragonal form II [3,4], and orthorhombic form III [5], which differ in the chain conformations and the packing of chains. The crystallization conditions of the various forms have been investigated in great detail [5–11], mainly on PB-1 samples prepared with Ziegler–Natta catalysts. The tetragonal form II is the kinetically favored morphology of PB-1 and generally obtained by melt crystallization [6,9,10,12]. Form II transforms into the thermodynamically stable form I when storage for several weeks at room temperature [1,6,7,13–16]. PB-1 is characterized by rapid crystallization of form II from melt but slow transformation to form I spontaneously and irreversibly [6,15],

accompanied with the notable enhancement of thermodynamical and mechanical properties, such as melting points, hardness, stiffness, and strength [7,13], which are beneficial to the improvement of performance of PB-1. The crystal form I' has similar structure to form I but is unstable when obtained directly from the melt, which is industrially unavailable. Although PB-1 has many interesting physical and mechanical properties, complex polymorphic behavior limits its commercial development. Therefore, understanding the kinetics of transformation from form II to form I in PB-1 is of great importance.

Crystal structures of form I and form II of PB-1 have been confirmed recently, where the R (right-handed helix) and L (left-handed helix) chains of (3/1) and (11/3) conformation are packed in the hexagonal and tetragonal unit cells alternately with the upward and downward directional disorder at each lattice site, respectively, with preservation of the helical hands during the transformation [17]. The two forms are related to the common plane of (110), where the resultant trigonal unit cell is parallel to that of the parent tetragonal unit cell via lateral

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movement of molecules [10,13,14]. The mechanism of this solid-to-solid phase transition from form II to form I is that the R and L 11/3 chains change to the 3/1 helices before pairing or the 11/3 to 3/1 conformation change occurring in the pair of the R and L 11/3 chains. In the actual transition, conformational change and translational motion of the chains may take place cooperatively so that the energy barrier to cross becomes as low as possible, which explains the formation of the twin structure of form I crystals [17,18]. This movement results in a transient structure, in agreement with the diffraction pattern during transformation observed by Li et al. [19]. For the form II to form I phase transformation kinetics, a first order transition including nucleation and growth has been established. Recent progress in this aspect rests on the separation of temperature effects on the nucleation and growth processes, respectively [20]. This transition in PB-1 is similar to the crystallization of small molecules. It is, therefore, possible to apply Tamman's two-stage nuclei development approach to confirm and quantify the relative rates of low-temperature nucleation and high-temperature growth of form II to form I phase transition in PB-1 as this approach has been extensively applied for the analysis of polymer nucleation and crystallization [21–23]. Actually, the crystal transformation time from form II to form I is mainly determined by the nucleation of form I (slower) in form II phase of PB-1, as mentioned by Men et al. It is well documented that the nucleation of form I crystals takes place most efficiently at 258 K–263 K, while the optimal temperature for the form I crystal growth is around 313 K [20]. In this way, by annealing the initial form II crystals first at 258 K–263 K for short time to induce the nuclei and then at 313 K to promote the growth of form I provides an ideal pathway for accelerating the formation of solid-phase in PB-1.

Nevertheless, the driving force that initiates the spontaneous transition from form II to form I at the molecular level is not yet clear. Further studies on the physics of the transformation are highly desirable in connection with advanced applications of PB-1. The two-step crystallization approach proposed by Li et al. [19] generates a region with a maximum transition rate, which locates at the growth front zone of the spherulites initially crystallized at high temperature, implying that the internal stress originated from the chain stretching at the boundary between crystal zone and amorphous zone plays an essential role in accelerating transformation from form II to form I. This brings two scenarios at the early stage of crystallization of form II: (1) Once the crystalline form II forms, the internal stress will emerge, and then the fast transformation from form II to form I will be initiated if the nuclei of form I crystals already exist. This then suggests that the growth of form II and the fast transformation into form I may take place simultaneously provided the crystal nuclei of form I already existed. (2) However, since the transformation from form II to form I starts at the growth front zone, the simultaneous growth of form II will be prohibited when the transformation occurs, and the increase of crystallinity of form II (if the crystallinity will increase) will be originated from newly formed crystalline from melt rather than growing from the existed crystalline form II. This involves the competition between the growth of form II and the transformation from form II to form I at the early stage of crystallization of form II. To understand these scenarios, experiments concerning the early formation of form II and the transformation from form II to form I are highly needed. However, till now, there is no available experimental data concerning the early growth of form II and the transformation from form II to form I at early stage since the crystallization of form II is very fast. Conventional differential scanning calorimetry (DSC) techniques are difficult to capture the early crystallization process of form II since form II may already form when cooling from melt at best few hundred K/min, which limits the investigation on the early formation of form II. Fast scanning chip calorimetry (FSCC) can realize high cooling capacity and short time constant, which permits isothermal measurement of melt-crystallization in a wide range of temperatures [24–27]. The cooling rate of FSCC can be as high as 4000 K/s, which greatly reduces the influence of non-isothermal cooling on the crystallization behavior [21,22,28–34].

This may help us capture the early formation of crystalline form II in PB-1.

In this study, we decomposed polymorphic transition in PB-1 from form II to form I into nucleation and growth steps of form I [20] by isothermal crystallization at T_C (isothermal crystallization temperature) for t_C (isothermal crystallization time) to obtain crystal form II with different crystallinity, and then immediately annealing at T_L (nucleating treatment temperature) for time t_L (nucleating treatment time) to induce nucleation of form I, and finally heating up to temperature T_H (isothermal transformation temperature) for time t_H (isothermal transformation time) to initiate the fast transformation from form II to form I. In this work, t_C ranges from 0 to 300s, t_L is set as 60s, and t_H ranges from 0 to 3 h, which allows us to investigate the isothermal time dependence on the formation of form II and the transformation from form II to form I. In order to avoid crystallization or transformation during heating and cooling, the heating and cooling rates were set as 1000 K/s. The rapid cooling at 1000 K/s followed by 258 K for 60s ensures nucleation of form I due to internal stress induced by unbalanced shrinkage of amorphous and crystalline phases because of their different thermal expansion coefficients. The crystallinity of form II was obtained via integrating the melting peak area of form II in DSC or FSCC measurement, and the fraction of crystal form I can be estimated from the ratio of melting enthalpy of form I to the total melting enthalpies of crystal form I and form II. To ensure the reliability of the experimental results, five independent measurements in DSC test and two independent measurements in FSCC test were performed for each sample. Good reproducibility is found for all the experiments. Crystal transformation kinetics study indicates that the competitive growth of form II and form I can be classified into three regimes: When t_C is small enough, the fast transformation from form II to form I does not take place, attributed to the extremely low crystallinity of form II and low degree of internal stress. With increasing t_C , the phase transition rate increases dramatically, and the maximum transition rate occurs as the C_{II} entering into the plateau region. When t_C further increases, the transition rate decreases and then reaches a plateau, resulting from the rearrangement of polymer chains and the increasing regularity of form II. Our results suggest that tiny internal stress is not enough to initiate the nucleation of form I. Only certain strength of internal stress and certain crystallinity of form II enable the nucleation of form I and then promote the transformation from form II to form I.

2. Experimental section

2.1. Materials

The PB-1 was produced by Lyondell Basell Industries with a trade name of PB0400M. The melt flow rate (MFR) and weight-average molecular weights are 16.4 g/10 min (463 K/2.16 kg) and 1.86×10^5 g/mol, respectively. The PB-1 pellets were dried under vacuum at 333 K for 24 h before use. Specimens for the FSCC analysis were prepared using a microtome to obtain thin sections with a thickness of 15 μ m, and then the thin sections were reduced in their lateral size to about 50–100 μ m using a scalpel with the aid of stereomicroscope.

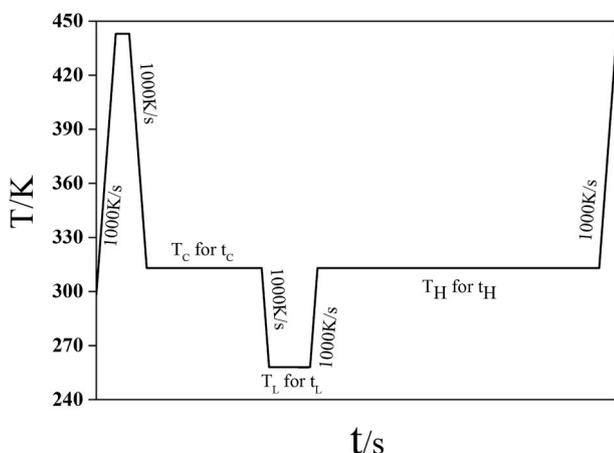
2.2. Instrumentation

Thermal analyses were performed with a DSC (DSC-Q2000 from TA Company) under the nitrogen atmosphere (50 mL/min). The instrument was calibrated with high purity indium as a standard to ensure the reliability of the data required. Isothermal crystallization kinetics of crystal form II was obtained from DSC measurements. In a typical measurement, about 5–10 mg samples were heated from 298 K to 453 K at a heating rate of 10 K/min and maintained at 453 K for 5 min to erase the thermal history. Then the samples were cooled to 298 K at a cooling rate of 0.033, 0.083, and 0.167 K/s (2, 5, and 10 K/min).

FSCC analyses were performed using a power-compensation

Mettler-Toledo Flash DSC 1 connected to a Huber intracooler TC100 for fast cooling and sub-ambient temperature operation. The calorimeters were purged with dry nitrogen gas at a flow rate of 35 mL/min. Before sample loading, the empty FSCC sensor was conditioned by multiple heating and cooling, and a temperature-correction/adjustment considering the specific thermal environment was performed according the instrument specification. Specimens were obtained by cutting thin sections of 10–15 μm thickness from the pellet, followed by decreasing their lateral size to about 100 μm . A thin layer of Wacker silicon oil AK 60,000 was spread on the membrane of the sample calorimeter and equally distributed using a single-hair tool to form a thin film before loading the specimen in order to improve the thermal contact between membrane and sample. The oil was then subject to repeated heating and cooling until absence of any drift of the heat-flow rate signal. Subsequently, the sample was placed on the sensor, with the first heating scan performed at a rate of 1 K/s to allow slow melting and adjustment of good thermal contact to the sensor. Experiments were performed on two samples using different sensors, to gain confidence regarding the observed results. In order to perform a proper measurement on our sample, self-nucleation experiments were performed (as shown in Fig. S1 of SI). We have checked two isothermal times (0.1s and 1s) and three starting temperatures (413 K, 443 K, and 473 K) to remove the thermal history. The measured heat flow for all the above conditions coincides with each other quite well, and therefore in this work, we use isothermal time 0.1s and starting temperature 443 K to remove the thermal history for all the samples [35,36]. Moreover, the cooling rate of ~ 100 K/s is enough to avoid crystallization during cooling. In this study, we use 1000 K/s as the cooling or heating rate for all the FSCC experiments. Due to fast heating and cooling (1000 K/s), cold-ordering and reorganization are avoided, and thus the enthalpy of melting is equal to the enthalpy of prior isothermal crystallization. Typically, the sample mass is in the range of 50 ng–300 ng. In our cases, the masses of two independent samples are 109 (± 5)ng and 56 (± 2.5)ng, respectively, which were estimated by comparing the measured absolute heat capacity of fully liquid iPB-1 with the expected specific heat capacity available in the ATHAS database [36] and comparing the measured with the expected heat-capacity increment on heating a fully amorphous sample at the glass transition temperature. Further information about instrumentation, instrument performance, and sample preparation is reported elsewhere [35–40]. Sample mass was also estimated by comparison of the absolute heat of crystallization in units of J, obtained in the FSCC, with the mass-specific heat of crystallization in units of J/g, obtained using a calibrated TA DSC-Q2000 on slow cooling at identical rates of 0.033, 0.083, and 0.167 K/s (2, 5, and 10 K/min). The error is within 5%, indicating good reproducibility.

The main thermal protocols are presented in Scheme 1. For the



Scheme 1. Schematic illustration of thermal treatment applied to PB-1.

isothermal crystallization study of form II, the samples were cooled to T_C (313 K, 323 K, 333 K) to crystallize for t_C (0–300s) after melting at 443 K to erase the thermal history. For the transformation study from form II to form I, the PB-1 samples were cooled to T_C (313 K, 323 K, 333 K) to isothermally crystallize for t_C (0–300s) after melting at 443 K for 0.1s to erase the thermal history [36], and then annealed at T_L (258 K) for t_L (60s) to nucleate, followed by annealing at T_H (313 K) for t_H (0–3 h) to initiate the transformation. The cooling and heating rates in all the processes are 1000 K/s. The annealed samples were then heated up to 443 K to obtain the melting curve, from which the crystallinity of form II and/or the contents of form II and form I can be calculated via integrating each melting peak area [41–43]. Melting peaks at 376 K–380 K (as shown in Fig. S1(a) of SI) and 386 K–390 K (as shown in Fig. S2 of SI) are assigned to be form II and form I respectively. The degree of the transformation can be manifested as the content of continuous transformed form I:

$$X_I = \frac{A_I / \Delta H_{id,I}}{A_I / \Delta H_{id,I} + A_{II} / \Delta H_{id,II}} \quad (1)$$

where A_I and A_{II} are the areas of form I and form II melting peaks, representing the melting enthalpies of form I and form II, respectively, and the melting enthalpies of ideal crystals in form I and form II are 141 J/g and 62 J/g [44], respectively.

3. Results and discussion

According to the two scenarios presented in the INTRODUCTION part, the early crystallization of form II and the instantaneous transformation from form II to form I at early stage are very important to understand the driving force that initiates the formation of form I. So in this part, we first investigate the isothermal crystallization kinetics of form II, and then we study the transformation kinetics from form II to form I in PB-1 with different crystallinities of form II. Finally, we will propose a possible mechanism of competition between the growth of form II and the transformation from form II to form I.

Isothermal crystallization kinetics of form II. To understand the early growth of crystal form II in PB-1, isothermal crystallization kinetics of form II was investigated via FSCC measurements. Typical FSCC curves of isothermal crystallization at 313 K for different t_C are shown in Fig. 1a. With increasing t_C , heat flow gradually exhibits a Gaussian-like crystallization exothermic curve, indicating the formation of crystals. The crystallization curves tend to reach a plateau when t_C is larger than ~ 12 s, implying that the crystallization may have completed at this moment. More reliable crystallization kinetic data are obtained from the melting measurements. Typical melting curves for different t_C are shown in Fig. 1b. It is seen that an endothermic peak appears at ~ 376 K with increasing temperature when t_C is larger than ~ 2 s, indicating the occurrence of crystalline form II. The crystallinity of form II (C_{II}) is then calculated via the ratio of measured melting enthalpy to the standard enthalpy of form II:

$$C_{II} = \frac{A_{II}}{\Delta H_{id,II}} \quad (2)$$

where A_{II} is the area of melting peak of form II, representing the melting enthalpy of form II, and the melting enthalpy of ideal crystal in form II is 62 J/g [44].

It is reported that isothermal crystallization temperature has a key effect on the crystallization kinetics of form II in PB-1, where increasing isothermal crystallization temperature may lead to increasing the lamella thickness of form II [45,46]. In this study, the isothermal crystallization processes at other temperatures ($T_C = 323$ K and 333 K) for different t_C are investigated, and the isothermal crystallization curves are shown in Fig. S3 of SI. With increasing t_C , heat flow also exhibits a Gaussian-like crystallization exothermic curve, which tends to reach a plateau when t_C is larger than ~ 13 s for $T_C = 323$ K and ~ 15 s for

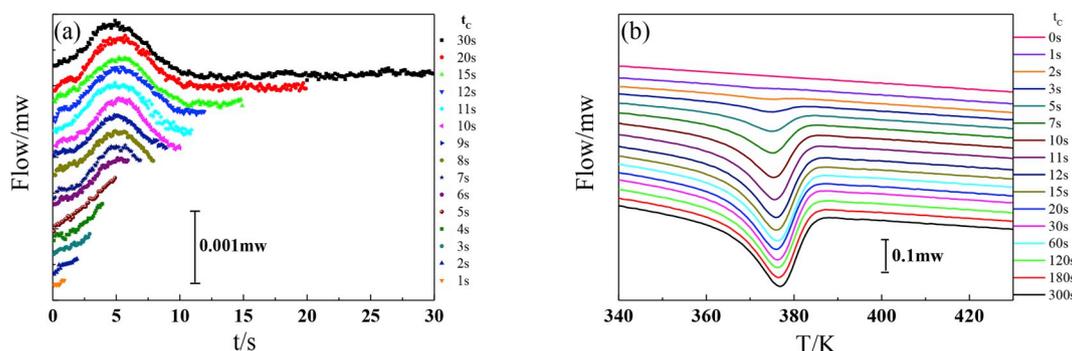


Fig. 1. The isothermal crystallization curves (a) and the melting curves (b) of PB-1 form II isothermally crystallized at 313 K for t_c after melting at 443 K for 0.1s.

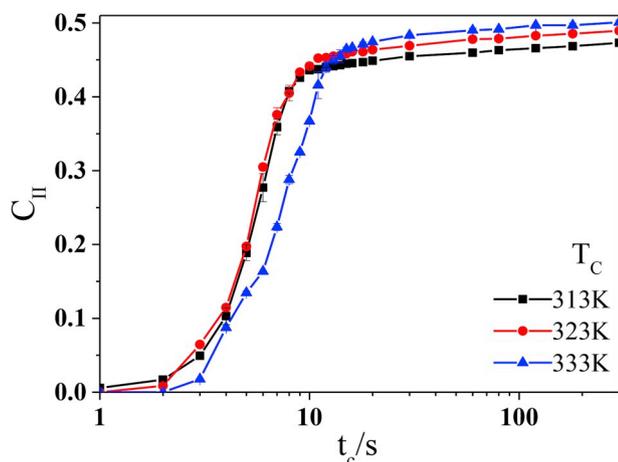


Fig. 2. The crystallinities of form II at different T_C .

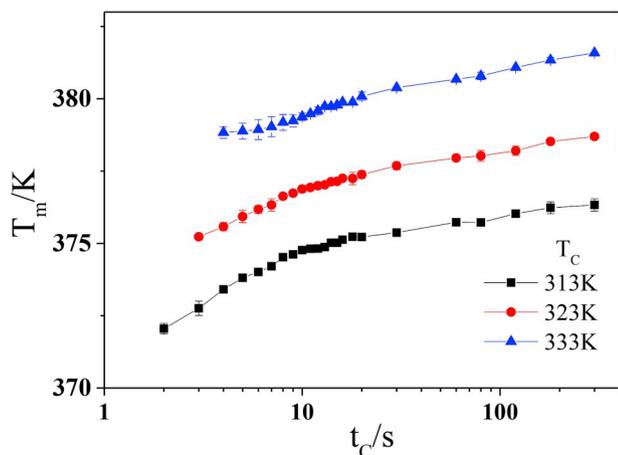


Fig. 3. The T_m of form II in PB-1 for different t_c when $T_C = 313$ K, 323 K, and 333 K, respectively.

$T_C = 333$ K, respectively. This indicates that, with increasing T_C , the growing rate of form II decreases, attributed to the weaker supercooling for higher T_C . The crystallinities of form II at different t_c and T_C are shown in Fig. 2. Take $T_C = 313$ K as an example, the C_{II} of form II first increases slowly when $t_c < \sim 2$ s, and then increases rapidly in the range from ~ 2 s to ~ 12 s, indicating the rapid growth of form II in this stage. The C_{II} of form II increases slowly again when t_c is larger than ~ 12 s, close to 44%, suggesting the rearrangement of polymer segments and the completeness of form II crystallization in this stage. It is interesting to see that, when t_c is between 2 and 8 s, the crystallization rate for $T_C = 313$ K and 323 K is higher than that for $T_C = 333$ K, which is mainly due to the decrease of supercooling degree at high T_C .

However, the crystallinity of form II at late stage for $T_C = 333$ K is higher than the others, attributed to the facile rearrangement of polymer chains at high temperatures. Moreover, the melting temperature (T_m) of crystalline form II increases with the increment of t_c and T_C , as shown in Fig. 3, implying increasing regularity and lamella thickness of form II at higher isothermal crystallization temperatures [45,46].

Nucleation and growth of form I. As illustrated in Figs. 2 and 3, by tuning the values of t_c and T_C , PB-1 with different C_{II} and different lamella thickness of form II can be obtained. Hence the competition between form II and form I can be studied by annealing these pre-crystallized samples at T_L (258 K) for t_L (60s) to nucleate and then annealing at T_H (313 K) for t_H (0–3 h) to initiate the fast transformation [20]. Our experiments have confirmed that maintaining 60s at 258 K does not cause amorphous or fully vitrified samples to crystallize into form II (as shown in Fig. S4 of SI). The annealed samples were heated up to 443 K to obtain the melting curve (as shown in Fig. S5 of SI), after which the content of form II and form I can be obtained via integrating each melting peak area and the degree of the transformation X_I can be calculated from Eq. (1). The values of X_I as functions of t_H for different t_c annealed at 313 K are shown in Fig. 4a. It is clearly seen that, when t_c is less than ~ 2 s, the transformation degree X_I is extremely low, even if the annealing time t_H is near 3 h. It should be noted that, when t_c is less than ~ 2 s, the crystallinities of form II (C_{II}) is no more than 4%. This indicates that lower crystallinity of form II is not enough to initiate the fast transformation from form II to form I. With increasing t_c , the crystallinities of form II increase, and then the transformation degree X_I almost increases linearly with increasing t_H , attributed to the increasing internal stress at high C_{II} . Interestingly, for $t_c = 3$ s, the values of X_I almost reach a plateau after $t_H = \sim 2$ h, suggesting that the initially formed form II has already transformed into form I, and the transformation from newly formed form II to form I is very slow since the newly formed form II does not have enough nucleus of form I due to lacking of treatment at low temperature.

Similarly, the values of X_I as functions of t_H at other isothermal crystallization temperatures ($T_C = 323$ K and 333 K) for different t_c are shown in Fig. S6 of SI. It is seen that the growing of X_I is slow when t_c is smaller than ~ 5 s for $T_C = 323$ K and ~ 7 s for $T_C = 333$ K. This indicates that the increasing isothermal crystallization temperature decreases the crystallizing rate of form II, and consequently decreases the transformation rate from form II to form I. The fast transformation and slow transformation are denoted as follows: the fast transformation occurs in the samples where the nucleation of form I is successfully induced by low temperature treatment after isothermal crystallization from the melt, while the slow transformation occurs in samples that have not been subjected to low temperature treatment after crystallization from the melt or that cannot induce form I nucleation at low temperatures due to insufficient internal stress in the system.

For different isothermal crystallization temperatures, the values of X_I increase almost linearly with increasing t_H , at least when t_H is less

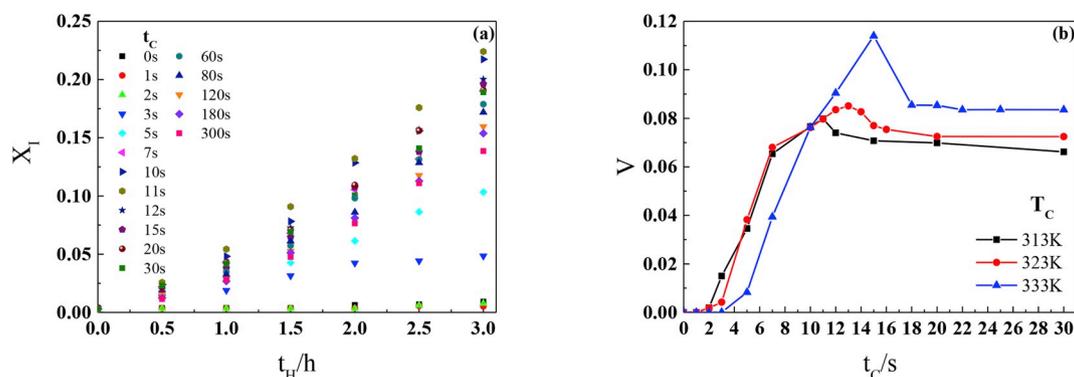


Fig. 4. The evolution of content of PB-1 form I as a function of t_H at 313 K after low-temperature treatment (a) and the corresponding V under different T_C (313 K, 323 K, 333 K) as a function of t_C after annealing at 258 K for 60s (b).

than 2 h. Then the slope (V) of the linear fitting of X_I as a function of t_H can be used to characterize the phase transition rate from form II to form I. The slope V as a function of annealing time t_C for different isothermal temperature is shown in Fig. 4b. It is clearly seen that there are three regimes with increasing t_C according to the variety of V .

- (1) When t_C is small enough, the phase transition rate V is nearly zero, indicating that the fast transformation from form II to form I does not take place, attributed to the extremely low crystallinity (less than $\sim 2\%$) of form II and the low degree of internal stress. It is well known that the internal stress locates at the boundary of the crystalline and amorphous regions during isothermal crystallization. The nucleation of form I is affected by the internal stress, but the latter is too small to induce the nucleation of form I when the crystallinity of form II is low enough although the low temperature nucleating process has been performed. This explains why the fast transformation from form II to form I does not happen when C_{II} is small enough. It should be noted that, even though the fast transformation does not happen in this stage, the crystalline form II will keep growing with increase of t_H (C_{II} will reach 44%–46% after 15s for all the studied samples), and these crystallites of form II will finally transformed into form I. However, due to lack of nuclei of form I, the transformation is very slow.
- (2) When t_C gradually increases, the phase transition rate V increases dramatically, and the maximum V occurs as the C_{II} entering into the plateau region (Fig. 2), corresponding to $t_C \sim 11$ s at 313 K, $t_C \sim 13$ s at 323 K, and $t_C \sim 15$ s at 333 K as shown in Fig. 4b. In this regime, the crystallinity of form II increases, and then the nuclei of form I form after low temperature treatment, and consequently the fast transformation from form II to form I initializes. However, the initial crystallinity of form II is still less than its capable maximum value. In this case, the transformation into form I and the growing of form II happen simultaneously but in different regions. However, the nucleation of form I only occurs in the already existed form II region, rather than the newly formed crystallite form II. Thus the fast transition happens in the originally existed form II region and will not stop until the originally existed form II has thoroughly transformed into form I. A clear evidence is also seen in Fig. 4a, in which the X_I reaches a plateau ($\sim 4\%$) after ~ 2 h for $t_C = 3$ s. It is interesting to see that the C_{II} for $t_C = 3$ s is also $\sim 4\%$ (Fig. 2). This indicates that the originally formed form II has transformed into form I in 2 h with a fast speed, and after that the slow transformation dominates the phase transition. It should be noted that the transition rate V for $T_C = 313$ K and 323 K is higher than that for $T_C = 333$ K, which is attributed to the high values of C_{II} for low T_C with fixed t_C , as shown in Figs. 2 and 4b.
- (3) When t_C further increases, the transition rate V decreases and then reaches a plateau. Moreover, with increasing T_C , V increases, accompanied with the increase of melting temperature of form I. In

this regime, the crystallinity of form II increases slowly, resulting from the rearrangement of polymer chains and the increasing regularity of form II (Fig. 2). In order to transform into more stable form I, the polymer chains in form II have to stretch themselves and change the conformation from 11/3 helical to 3/1 helical structure. However, the increasing regularity of form II makes the chains need more energy to realize the transformation into form I. Therefore, with increasing t_C , the regularity of form II increases, and then the transition rate decreases. Nevertheless, the transition rate is still much faster than that in the later stage of regime II since the nuclei of form I have been formed in all the form II regions. With increasing T_C , the transition rate increases due to the increasing lamella thickness and increasing the difference between crystallization and annealing temperature, agree well with that proposed by Men et al. [20,45].

The transition mechanisms at different t_C and T_C are schemed in Fig. 5. The gray dotted ellipses indicate the boundary between the crystallite form II and the amorphous region where the internal stress exists and the nucleation of form I may happen. The green solid circles mark the place where the nuclei of crystal form I locate. In the first regime, the internal stress is too small to induce the nucleation of form I even though the low temperature nucleating process has been performed. Consequently, high temperature annealing does not promote the transformation from form II to form I but only leads to the growing of form II. Thus, only slow transformation occurs due to lacking of nuclei of form I. In the second regime, the crystallinity of form II increases and the internal stress also increases, which is enough to initiate the nucleation of form I after low temperature treatment. Thus the fast transformation happens. However, after all the originally existed form II has transformed into form I, the slow transformation dominates since there is no nuclei of form I in the newly formed form II region. In regime III, the crystallinity of originally formed form II is 44%–46%, close to its capable maximum value of form II when isothermal crystallization at 313 K. After low temperature treatment, the nuclei of form I have been formed in all the form II regions, leading to the fast transformation from form II to form I. Our results suggest that tiny internal stress is not enough to initiate the nucleation of form I. Only certain strength of internal stress and certain crystallinity of form II enable the nucleation of form I and then promote the transformation from form II to form I.

4. Conclusion

In this work, the effect of the crystallinity and lamella thickness of form II on the nucleation and growth of form I is investigated by using FSCC. The heating and cooling rates were set as 1000 K/s to avoid any crystallization or transformation during heating and cooling. Then the polymorphic transition in PB-1 from form II to form I is decomposed into nucleation and growth steps of form I by isothermal crystallization

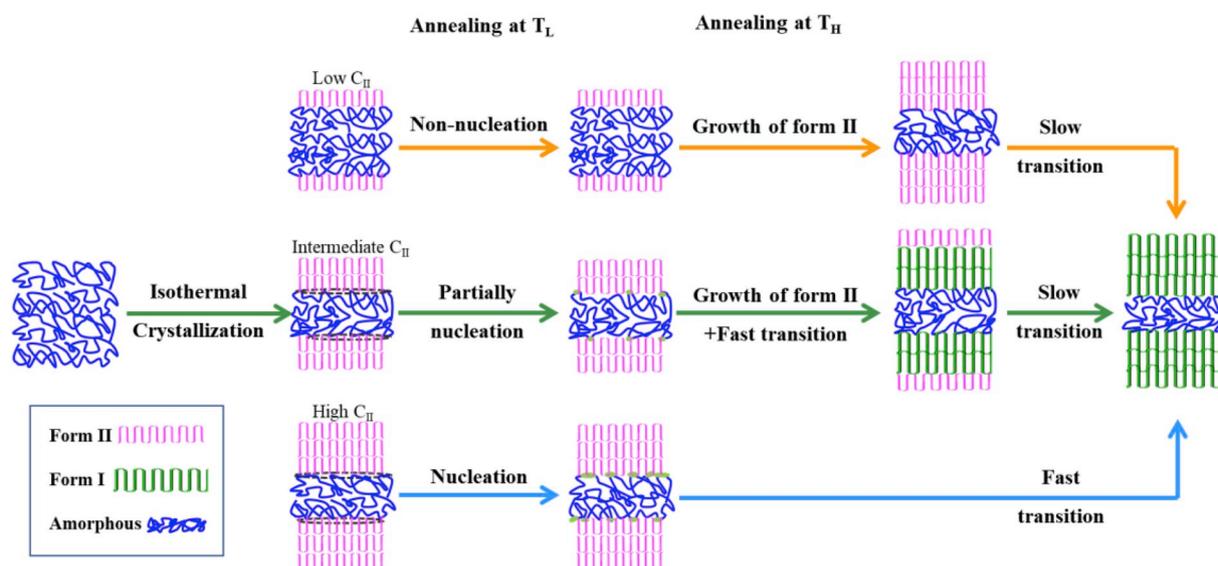


Fig. 5. Schematic representation of the competitive growth of form I and form II.

at T_C for t_C to obtain crystal form II with different crystallinity, and immediately annealing at T_L for t_L to nucleate form I, and finally heating up to T_H for t_H to initiate the transformation. The crystallinity of form II and the fraction of crystal form I can be estimated from integrating the melting peak area of form II and form I in DSC or FSCC measurement. There are three regimes for the competitive growth of form II and form I. When t_C is small enough, the fast transformation from form II to form I does not take place, attributed to the extremely low crystallinity of form II and low degree of internal stress. With increasing t_C , the phase transition rate increases dramatically, and the maximum transition rate occurs as the C_{II} entering into the plateau region. This suggests that only certain strength of internal stress and certain crystallinity of form II can initialize the low-temperature nucleation of form I and then promote the transformation from form II to form I. However, after all the originally existed form II has transformed into form I, the slow transformation dominates since there is no nuclei of form I in the newly formed form II region. When t_C further increases, the transition rate decreases and then reaches a plateau, resulting from the rearrangement of polymer chains and the increasing regularity of form II. As expected, thicker lamellar form II always benefits to the transformation into form I. But surprisingly, the increasing crystallinity of form II does not always benefit to the transformation from form II to form I. In the plateau regime, the crystallinity of form II increases slowly, combined with the increase of the regularity of form II. However, the polymer chains in regular form II needs more energy to change the conformation from 11/3 helical to 3/1 helical structure than those in the imperfect crystalline form II, leading to the negative impact on the transformation from perfect form II into form I. Our results will shed new light on the competitive mechanism between the growth of crystalline form II and the transformation from form II to form I in PB-1.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2019.03.051>.

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